First-Principles Transport Properties for Combustion Modeling

Scientific Achievement

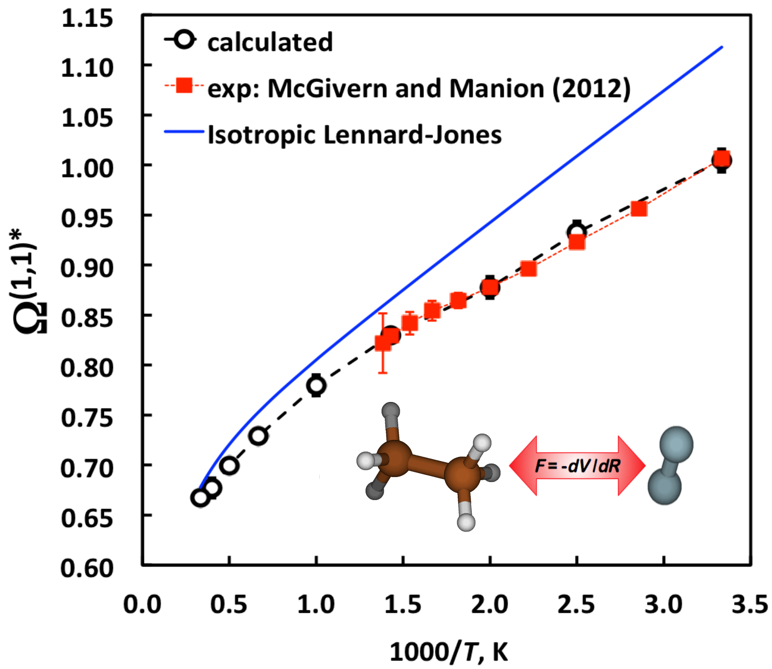
We demonstrated that very accurate transport properties can be calculated using classical trajectories and ab initio-based force fields.

Significance and Impact

Detailed chemical models of complex gas phase systems require thousands of kinetic and molecular parameters, most of which are either unknown or poorly known. Of these, transport properties are among the least well characterized. Our method provides a means of quantitatively predicting transport for thousands of previously uncharacterized species.

Research Details

- The collision integrals $\Omega^{(l,s)}$ are directly related to bulk transport properties (diffusion, viscosity, etc.).
- We calculate exact classical $\Omega^{(l,s)}$ using full-dimensional trajectories and ab initio-based force fields. The missing quantum effects are negligible, even for light species.
- The usual Lennard-Jones model for $\Omega^{(l,s)}$, in contrast, neglects inelasticity and anisotropy and has unrealistic repulsive forces. We quantified the errors due to these approximations.



The calculated collision integral for ethane + N_2 is in quantitative agreement with measured values of McGivern and Manion (NIST). This calculation has no adjustable parameters. The simple Lennard-Jones model is in fair agreement at high temperature, with larger errors are low temperatures.

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A. W. Jasper, E. Kamarchik, J. A. Miller, and S. J. Klippenstein, *J. Chem. Phys.* **141**, 124313 (2014).

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